SECOND QUARTERLY REPORT

DEVELOPMENT OF SECONDARY CADMIUM-OXYGEN CELLS FOR SPACECRAFT APPLICATIONS

(1 JULY 1967 - 30 SEPTEMBER 1967)

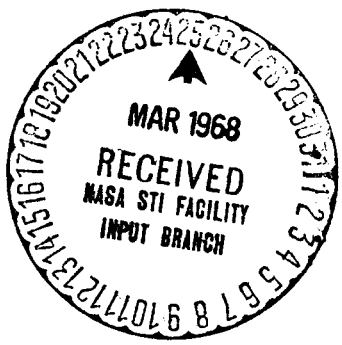
CONTRACT NO. NAS 5-10384

for

GODDARD SPACE FLIGHT CENTER

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

GREENBELT, MARYLAND



APPROVED BY:

R. A. Powers, Director

CONSUMER PRODUCTS DIVISION
RESEARCH LABORATORY
PARMA, OHIO

ABSTRACT

Parallel programs exploring cell characteristics of cadmium-oxygen cells have been continued through this report period. A two-electrode cell structure utilizing an oxygen electrode purchased from the American Cyanamid Company and a Union Carbide electrodeposited cadmium electrode has given rather poor cycle life on a two-hour charge/two-hour discharge regime. The cell failure has been traced to oxygen electrode deterioration. The mode of failure has been severe oxygen electrode polarization on both charge and discharge. Reasons for the oxygen electrode failure have not been established, but may be a result of oxygen evolution during charging of the cell. Cycle life has ranged from as low as 25 cycles to about 200 cycles for this cell type. A three-electrode cell utilizing a Union Carbide oxygen electrode, a Union Carbide electrodeposited anode, and a third electrode for charging has also shown oxygen electrode limitation, but has given cycle life in the range of 200 to 500 cycles on the two-hour charge/two-hour discharge regime. Cell tests have been complete discharge tests (initially to 0.2 volt and later to 0.4 volt) at constant current.

Tests with both types of cells are being run on a 24-hour charge/24-hour discharge regime. No problems or failures have occurred to date. The two-electrode cell has completed 15 cycles and the three-electrode cell has completed 39 cycles as of October 1st.

Cells have been built for 0°C and 40°C tests which will be started soon.

The cadmium electrodeposition process has been used to produce anodes with approximately four times the capacity of the original stock anodes. Cycle life and capacity characteristics are being evaluated.

* * * * * *

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

INTRODUCTION

Work conducted to date has continued to show the feasibility of recharging the cadmium-oxygen system. Work has continued on parallel programs exploring a two-electrode and a three-electrode experimental cell construction. In the two-electrode cell, the oxygen electrode used was purchased from the American Cyanamid Co. With the two-electrode cell structure, the oxygen electrode is used for both charge and discharge. The three-electrode cell is constructed so that the oxygen electrode is idle during the charge cycle while a third inert electrode carries the charging current. Union Carbide oxygen electrodes are normally used in the three-electrode cells. The cadmium electrodes have been made by Union Carbide's electrodeposition process.[1]

Two-electrode cells being tested on a two-hour charge/two-hour discharge regime have shown relatively short cycle life which has been traced to poor oxygen electrode performance. A number of experiments and cell modifications have been attempted in an effort to isolate the problem. Similar cells on the 24-hour charge/24-hour discharge regime have not shown this deficiency to date.

During this period all tests have been to essentially complete discharge. Initially 0.2 volt was used as the end of test cut-off voltage, but since the end of discharge voltage drops very sharply, 0.4 volt cut-off was adopted as standard. This change makes very little change in cell capacity.

DISCUSSION

A. Description of Components

1. Oxygen Electrodes

The oxygen electrodes used in cells tested during this report period are the same as those used previously and reported in our First Quarterly Report. One is the Union Carbide "fixed-zone" electrode which consists of an electrochemically active carbon layer applied to porous metal backing. Because of its susceptibility to damage from oxygen evolution which occurs during charging, this electrode may be used only when a third electrode serves as the charging electrode.

The other oxygen electrode was purchased from the American Cyanamid Company and is designated as type "Lab-40" with A-2 backing. This electrode is composed of a catalyzed electrochemically active material, bonded with "Teflon", embedded in a gold plated nickel screen collector, and backed with a porous material. Various backing materials with different porosities are available. Electrodes used to date have had a backing designated as type A-2. This electrode structure should be resistant to damage from oxygen evolution during the charging cycle, eliminating the need for a third or charging electrode.

2. Cadmium Electrode

The cadmium electrodes used have all been made by the patented Union Carbide electrodeposition process as described in our First Quarterly Report. Electrodes used in the majority of tests had a nominal capacity of 0.031 amp-hr/cm^2. Recently a few electrodes have been made with 0.121 amp-hr/cm^2. Electrodes can be made on a base of nickel, copper, silver or other material. Electrodes used to date have been plated on 40 x 40 mesh nickel screen with 0.007 inch diameter wire.

3. Electrolyte

The electrolyte used is 40 percent by weight (10 N) potassium hydroxide prepared from reagent grade pellets.

4. Separators

Two types of separators are used in our cell construction. One type is a special woven polypropylene mat obtained from The Lamports Company. This material is designated as "waffle weave" S/7700. Its wide open structure makes it suitable for the charging electrode separator where oxygen escape paths are necessary. The other separator is a non-woven nylon fiber felt. This material is used as the cadmium electrode separator. When wet with electrolyte, it provides an efficient barrier to oxygen gas bubbles from the charging electrode. This material has been obtained from the Pellon Corporation and is identified as No. 10194C.

5. Cathode Current Collector

The American Cyanamid electrode is capable of serving as its own current collector due to the embedded gold plated nickel screen. It is also rigid enough to need very little support on the gas side. The Union Carbide electrode is also capable of serving as its own current collector at low current densities due to the porous metal backing. It is, however, a very thin and flexible electrode, and needs support on the gas side to prevent collapse into the space provided for gas circulation. Adequate support and better current collection is obtained by the use of an expanded nickel grid in the gas space. Material designated as 5 Ni 15 2/0 obtained from Exmet Corporation has been used for this purpose.

B. Experimental Unit Cell Construction

The experimental unit cells used to evaluate the cadmium-oxygen system are essentially the same as those reported in our First Quarterly Report. These are the three-electrode unit cell and the two-electrode unit cell. A detached view of each of these unit cell types is reproduced from the First Quarterly Report for the convenience of the reader. Figure 1 is a detached view of a standard three-electrode cell and Figure 2 is a detached view of a two-electrode cell.

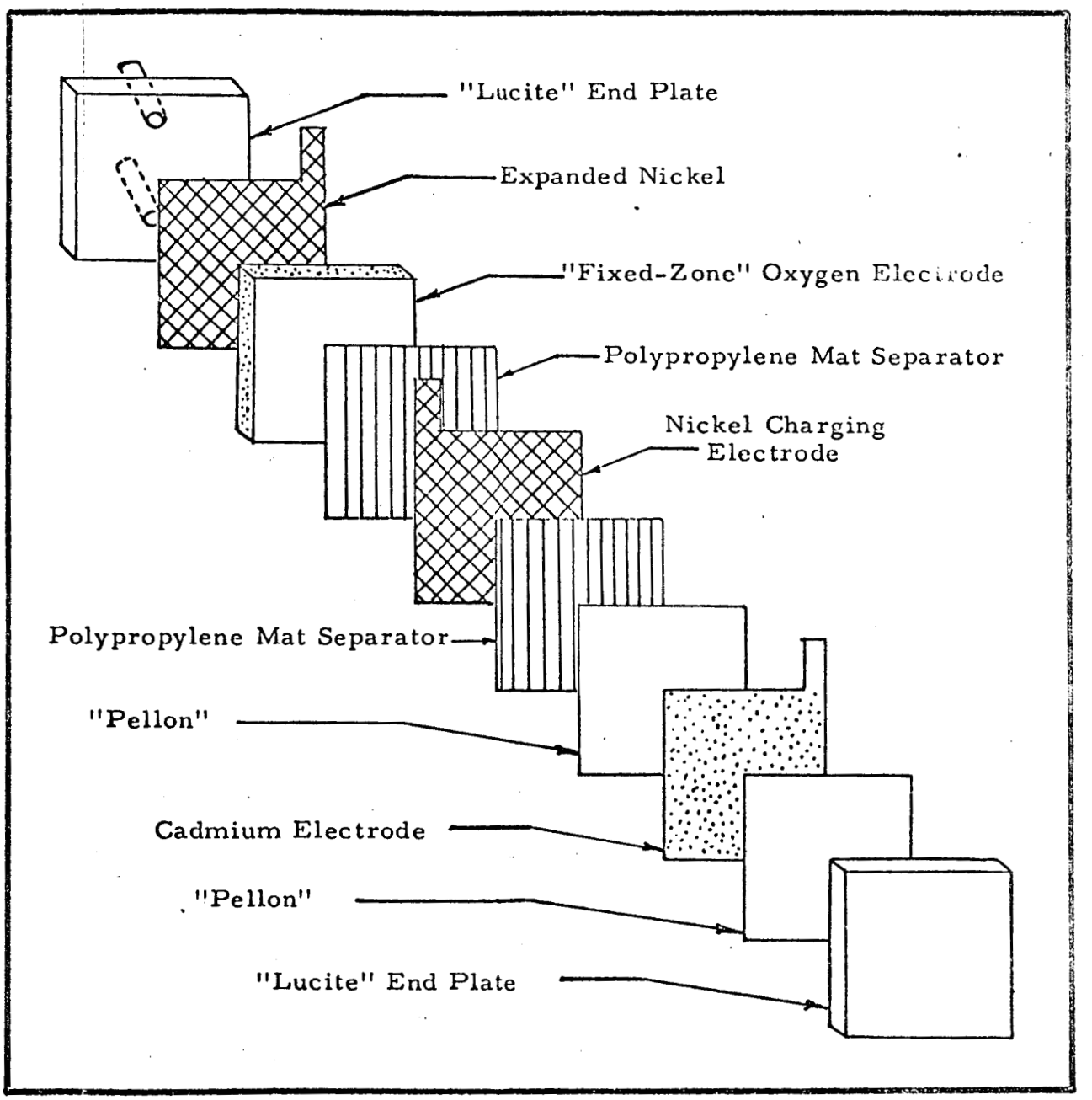
Several construction variations have been attempted. For the three-electrode system, with reference to Figure 1, these were as follows:

a. The charging electrode was moved from between the anode and cathode to the opposite side of the anode. This allows much closer spacing between the anode and cathode so that the cell discharges at a higher voltage.

b. The same arrangement as in a. above, but with the addition of two layers of "Zephyr" between the charging electrode and the anode. "Zephyr" is a trademark for a cellulose casing material made by Food Products Division, Union Carbide Corporation. This provides positive separation of the anode from oxygen generated at the charging electrode.

FIGURE 1.

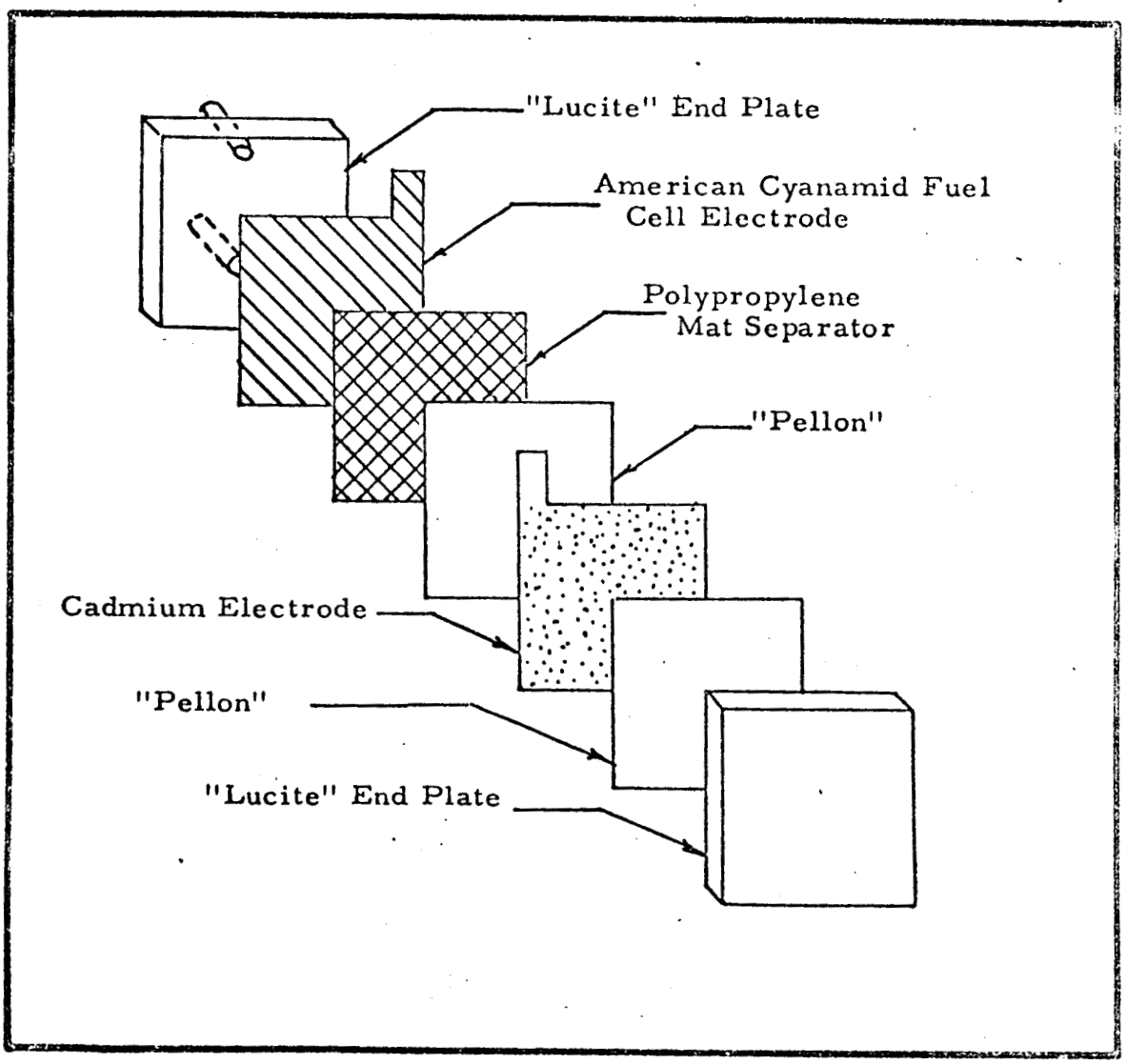
STANDARD CONSTRUCTION OF UNIT CELL IN THREE-ELECTRODE SYSTEM



C-3668

FIGURE 2.

STANDARD CONSTRUCTION OF UNIT CELL IN TWO-ELECTRODE SYSTEM



C-3669

c. An attempt was made to operate a cell without the "Pellon" anode separator, but with the polypropylene charging electrode separator retained for cell spacing purposes.

Construction variations made in the two-electrode system, with reference to Figure 2 were:

a. An attempt was made to operate a cell without the "Pellon" anode separator as a parallel experiment to c. above.

b. A cell was constructed with a double thickness of polypropylene separator between the anode and cathode in an attempt to improve oxygen escape during the charge cycle.

c. A cell was constructed with the normal anode to cathode spacing, but the polypropylene separator was left out. To maintain normal spacing a peripheral "Lucite" spacer was used. This is to provide a completely clear path for oxygen evolution during charging.

C. Unit Cell Performance

1. Three-Electrode System

With the cell structure shown in Figure 1, cycle life has not been as good as we had expected from work reported in the First Quarterly Report. With the Union Carbide electrode, cycle life on two-hour charge/two-hour discharge regime has been between 200 and 500 cycles. However, at reduced capacity (50 percent or less) these cells have continued cycling beyond 700 cycles. Except for a few cases where poor restraint of the cadmium electrode has been the cause of failure, the oxygen electrode has slowly deteriorated. We are not able at this time to explain the early failure of these electrodes. Cell No. 21 of Table I is typical of the standard construction.

Several cells have been tested wherein the third or charging electrode has been removed from between the anode and cathode, and placed behind the anode. In this construction, the anode and cathode are much closer together

TABLE I.

COMPARISON OF CONSTRUCTION VARIATIONS IN THREE-ELECTRODE SYSTEMS

Performance Data Is Average of All Cycles Completed

Variation	Cell No. 16 Charging electrode behind Cd	Cell No. 18 No "Pellon" Separator	Cell No. 19 Charging Electrode behind Cd; 2 layers "Zephyr" between Cd & charging electrode.	Cell No. 21 Standard construction (O_2-Ni-Cd)
Cycles	490	75	30	27
Cause of Failure	O_2 Electrode Wet	Short Circuit	Hot Spot	Still Going
Cd Weight (lb.)	0.0186	0.0186	0.0186	0.0186
Component Weight[1] (lb.)	0.142	0.134	0.152	0.157
Average Input (Ampere-Hours)	1.84	1.68	1.52	1.66
Average Output (Ampere-Hours)	1.69	1.65	1.50	1.64
Average Discharge Voltage (Volts)	0.81	0.80	0.795	0.79
Average Component Capacity (Watt-Hours per pound)	9.65	9.85	7.84	8.26
Average Current Density (ma/cm^2)	14.85	14.6	13.6	13.8

[1] Components consist of oxygen electrode, electrolyte, cadmium electrode.

resulting in about 50 to 70 millivolts higher operating voltage during discharge. The cadmium electrode appears to charge readily from the reverse side with anodes up to 0.084 inch thick. A typical cell of this construction is No. 16 in Table I.

In a cell with the charging electrode behind the anode and with two layers of "Zephyr" between the charging electrode and the anode, the internal resistance on charging was very high. Instead of gaining capacity by protecting the cadmium from oxygen, we were unable to achieve full charge and had low capacity. Cell No. 19 of Table I shows the average behavior of this cell.

To experimentally determine the effects of using no "Pellon" anode separator in the standard construction, Cell No. 18 was made up. Spacing between the anode and cathode was maintained by the polypropylene mat separator. Only a very slight gain in operating voltage was noted. As expected, however, there was a severe shortening of cycle life due to loss of cadmium from the anode. Eventually the cell was shorted by the accumulation of cadmium at the bottom of the cell. This cell was No. 18 in Table I.

2. Two-Electrode System

A two-electrode cell was built as a parallel experiment for the three-electrode cell with no "Pellon" separator around the anode (see Cell No. 18 in Table I). This cell (No. 24 in Table II) gave results which were very similar to those obtained with the three-electrode system.

With American Cyanamid electrodes built into the two-electrode unit cell, cycle life on the two-hour charge/two-hour discharge regime has been from 25 cycles to 200 cycles. The failure mode has been rather odd and is not yet completely understood. Cells when first started will cycle normally when charged at constant current to a voltage cut off of 1.65 volts Cd-O_2. After from 10 to 20 cycles, the capacity becomes less and less until in a short time the cells are charging to cut-off voltage in less than five minutes. If left alone, these cells sometimes recover to full capacity, and then go through another period of capacity reduction. Increasing the charging cut-off voltage also will cause the cell to recover for a time. Raising the charge cut-off voltage 0.10 volt may bring the capacity back to nearly normal for from 5 to 20 cycles.

TABLE II.

COMPARISON OF CONSTRUCTION VARIATIONS IN THE TWO-ELECTRODE SYSTEM

Performance Data Is Average of All Cycles Completed

	Cell No. 20	Cell No. 24	Cell No. 27	Cell No. 32
Variation	2 polypropylene spacers between electrodes	No "Pellon" on cadmium electrode	No spacers in cell; spacing same as with one spacer	Standard Construction (Figure 2.)
Cycles	157	86	153	41
Cause of Failure	Cathode polarization.	Anode sloughing	Still going	Cathode polarization
Cd Weight (lb.)	0.0192	0.0205	0.0236	0.021
Component Wt. (1) (lb.)	0.152	0.132	0.181	0.113
Average Input (Ampere-Hours)	1.08	1.76	1.76	1.87
Average Discharge Voltage (Volts)	0.83	0.84	0.82	0.84
Average Output (Ampere-Hours)	1.05	1.72	1.76	1.78
Average Component Capacity (Watt-Hours per pound)	5.74	10.95	8.02	13.22
Average Current Density (ma/cm^2)	17.5	18.7	18.9	16.0

(1) Components consist of oxygen electrode, electrolyte, cadmium electrode.

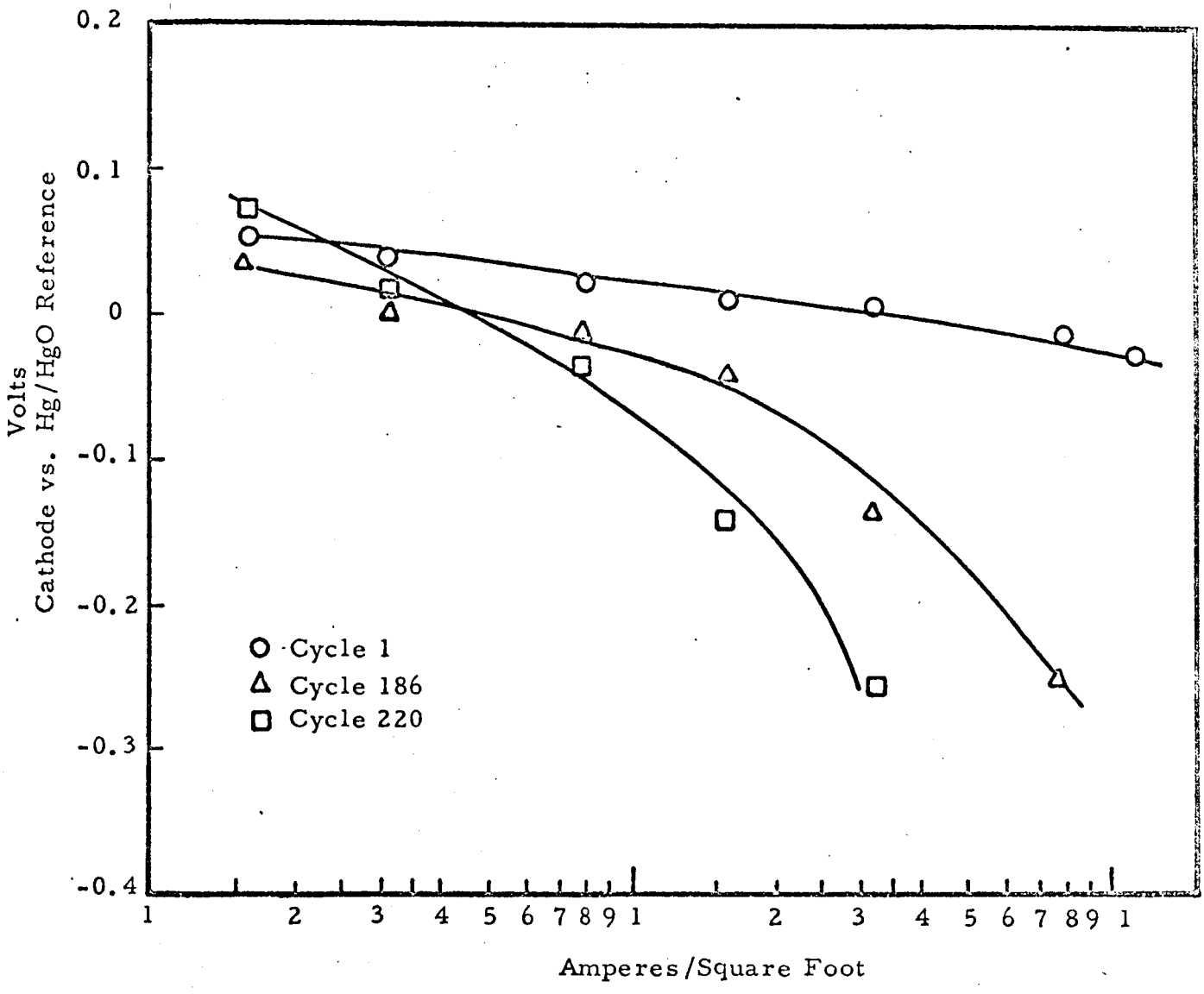
This ability to recover to nearly full capacity led us to believe the fault might be a large gas bubble trapped in the mesh of the polypropylene separator. To test this possibility, a cell was constructed with double the normal interelectrode spacing and with two polypropylene separators to give a better gas escape path. A second cell was also built with normal spacing but with no polypropylene spacer as another means of providing for better gas escape. These cells Nos. 20 and 27, respectively, are compared to a standard two-electrode cell No. 32 in Table II. These two tests showed that the problem was not caused by gas bubbles in the polypropylene separator. However, much more efficient oxygen evolution is obtained when the polypropylene separator is not used.

Polarization studies of Cell No. 20 have shown that the oxygen electrode is deteriorating with time as shown in Figure 3. The cell behavior throughout its life is depicted in Figure 4. Through cycle 27, the charge was cut off at 1.65 volts, but by then charge input was getting quite low so on cycle 28 the cut off was raised to 1.75 volts. Again at 90 cycles it was necessary to raise the charge cut off to 1.80 volts.

More information is gained from Cell No. 17 which was tested on the Union Carbide Computer Test Facility. The test was set up to charge at 0.8 ampere constant current to 1.75 volts cut off or 2.0 hours, and to discharge at 0.8 ampere constant current to 0.4 volt or 2.0 hours. A mercury/mercuric oxide reference electrode was included in the cell so that the performance of the individual electrodes is known. Table III shows the performance of the cell through 16 cycles respectively. Through the first four cycles, the cadmium was not completely charged and the cut-off voltage was not reached on either charge or discharge. Figure 5 and Figure 6 show the cell and electrode potentials for the first and third cycles. On the fifth and all succeeding cycles, the cell reached cut-off voltage on charge so that less than 1.6 amp-hr of charge was returned to the cell. The discharge capacity did not go below 1.6 amp-hr until the seventh cycle, however, indicating an anode capacity somewhat greater than 1.6 amp-hr.

FIGURE 3.

IR FREE POLARIZATION OF OXYGEN ELECTRODE IN CELL NO. 20



C-3751

FIGURE 4.

CHARGE AND DISCHARGE CHARACTERISTICS OF THE CELL WHOSE CATHODE POLARIZATION IS SHOWN IN FIGURE 3.

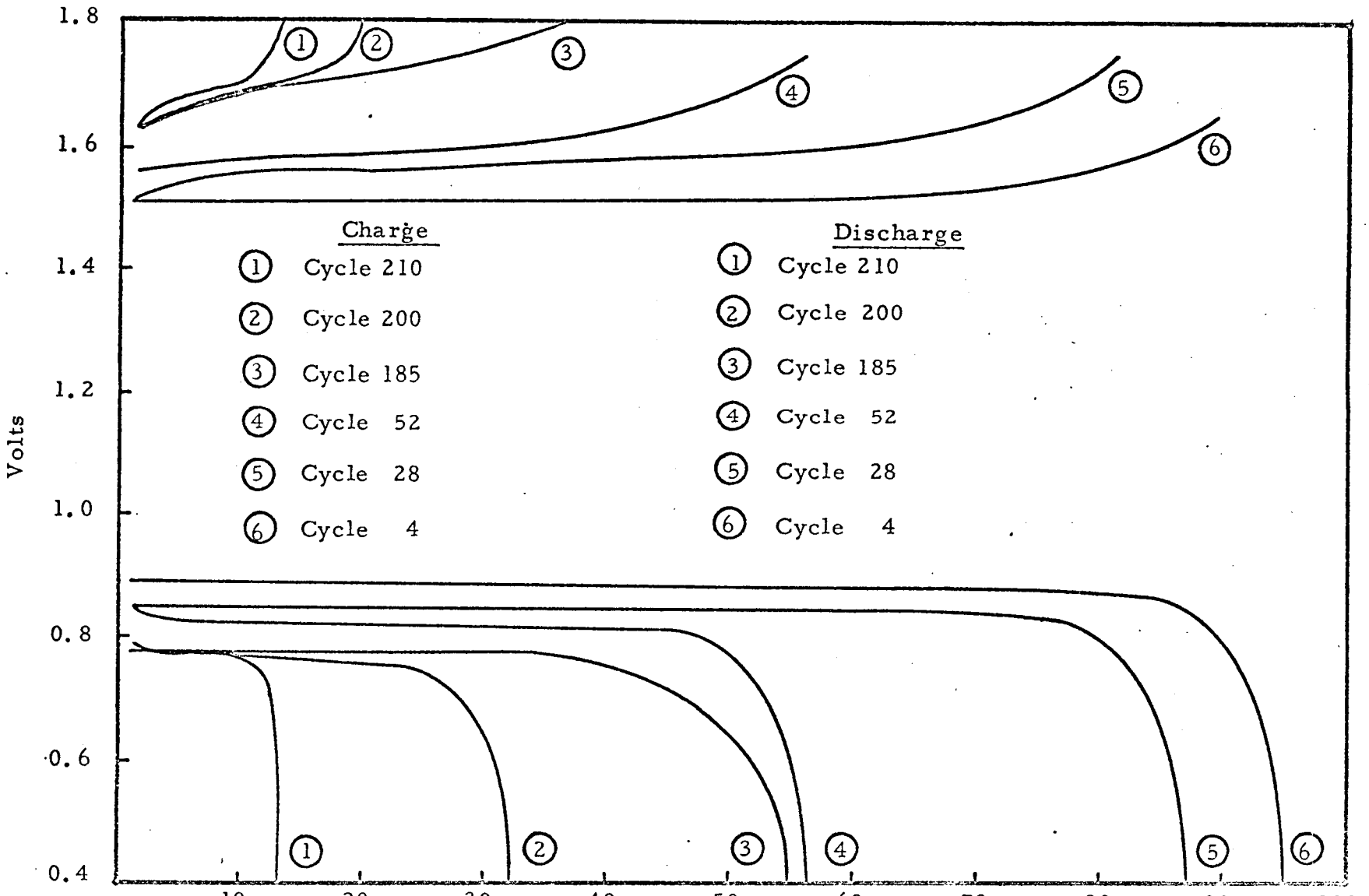


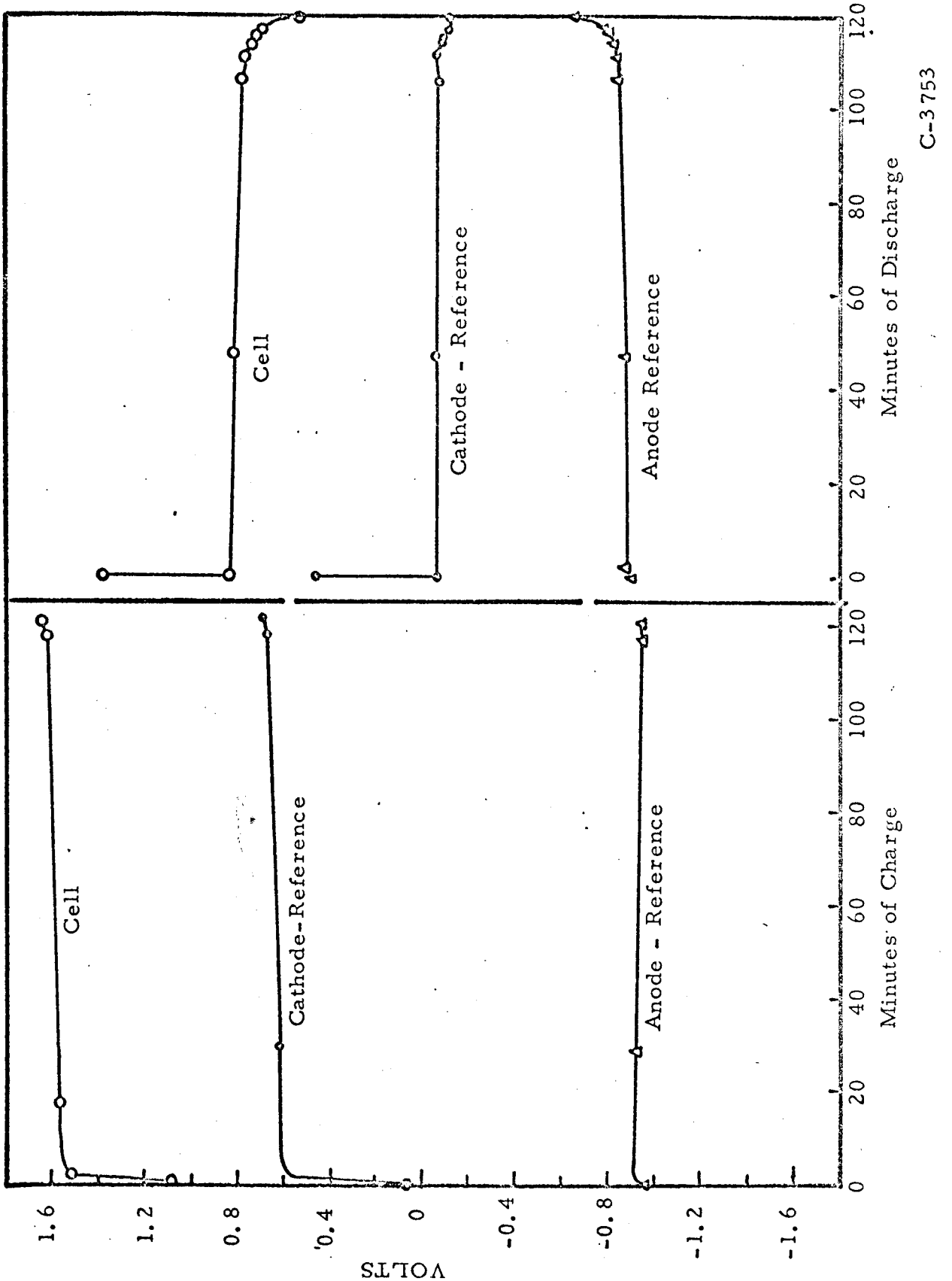
TABLE III.

PERFORMANCE OF THE TWO-ELECTRODE SYSTEM - CELL NO. 17

Cycle	End of Charge Voltage	Avg. C. V.	Charge Time (Hours)	Amp-Hr. Charge	End of Discharge Voltage	Avg. D. V.	Discharge Time (Hours)	Amp-Hr. Discharge	Comp. W-Hr/lb.
1	1.627	1.560	2.00	1.60	0.541	0.802	2.00	1.60	9.93
2	1.670	1.571	2.00	1.60	0.693	0.793	2.00	1.61	9.83
3	1.712	1.577	2.00	1.58	0.698	0.786	2.00	1.60	9.70
4	1.745	1.583	2.00	1.58	0.685	0.780	2.00	1.61	9.70
5	1.750	1.591	1.97	1.57	0.653	0.770	2.00	1.60	9.54
6	1.750	1.600	1.95	1.55	0.534	0.762	2.00	1.60	9.37
7	1.750	1.606	1.94	1.54	0.400	0.753	1.96	1.57	9.15
8	1.750	1.613	1.92	1.53	0.400	0.751	1.92	1.55	9.00
9	1.750	1.626	1.88	1.49	0.400	0.744	1.84	1.48	8.53
10	1.750	1.638	1.80	1.43	0.400	0.740	1.81	1.45	8.30
11	1.750	1.643	1.75	1.39	0.400	0.615	1.41	1.13	5.35
12	1.750	1.717	1.39	1.10	0.400	0.592	1.57	1.27	5.82
13	1.750	1.732	1.39	1.11	0.400	0.599	1.37	1.10	0.00
14	1.750	1.752	0.02	0.01	0.400	0.513	0.04	0.03	0.00
15	1.750	1.767	0.01	0.00	0.400	0.479	0.02	0.01	0.00
16	1.750	1.758	0.01	0.00	0.400	0.459	0.02	0.01	0.00

FIGURE 5.

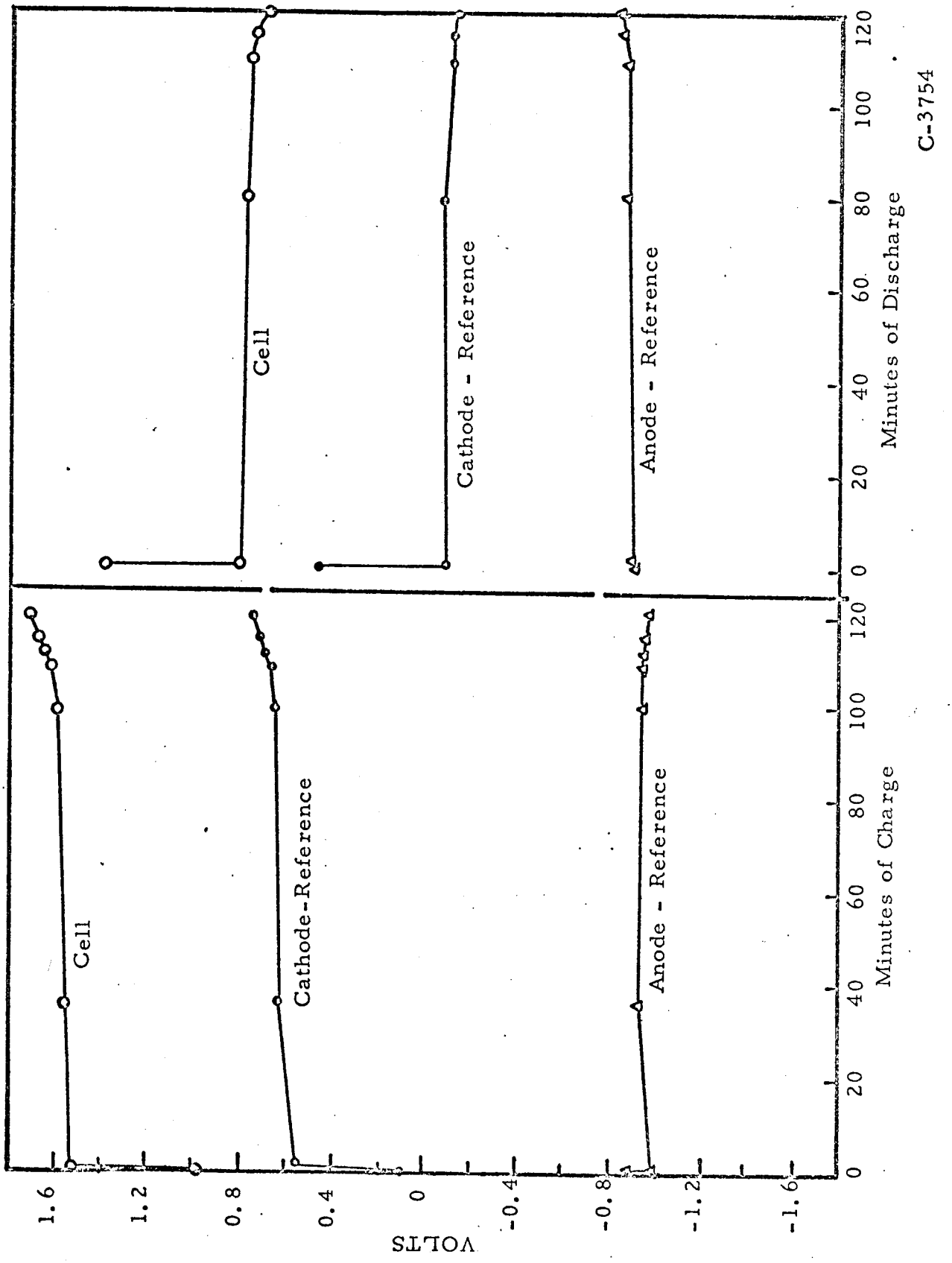
CELL NO. 17 - FIRST CYCLE



C-3753

FIGURE 6.

CELL NO. 17 - THIRD CYCLE



In Figure 7 the charge curves show that by cycle 9, the oxygen electrode charge potential is normal and the electrode is reaching full charge in less than two hours. The discharge curves show the oxygen electrode polarizing severely with time and limiting the discharge. When one observes only symptoms measurable at the terminals of the cell, it would seem that in the short charge time the anode is not becoming fully charged. In reality, however, the reference electrode readings show that the anode is never fully discharged, and that the cathode is polarizing severely on discharge each cycle. Then the smaller amount of charge needed by the anode limits the charge cycle.

Further deterioration of the oxygen electrode at cycle 13 is shown in Figure 8. The discharge potential of the oxygen electrode is lower and polarization to failure occurs sooner. Also, we note that the initial charging potential of the oxygen electrode has increased from about 0.63 volt to 0.78 volt versus Hg/HgO. This puts the cell charging voltage very near the cut off of 1.75 volts at the very start of the charge cycle. In the next cycle the charge voltage reaches the cut-off voltage within two minutes as shown in Figure 9 (cycle 14). The oxygen electrode ability to function on discharge has also been lost.

We do not know what causes the breakdown of the American Cyanamid electrode, but we are trying to find out. Cells have been built with a third charging electrode so that the "Lab-40" electrode is isolated during charge in the same way the Union Carbide T-2 electrode is used. Only a very few cycles have been completed to date, so that no conclusions may be reached as yet.

3. 24-Hour Charge/24-Hour Discharge Regime

Both the two-electrode and three-electrode system have been tested on a 24-hour charge/24-hour discharge regime. The cells were first cycled on the two-hour charge/two-hour discharge regime to characterize them with respect to previous cells. Average performance of these cells on the two-hour regime is shown in Table IV. Cell performance on the 24-hour regime is shown in Tables V and VI. As is to be expected, discharge voltages are higher and the cadmium electrode efficiency is better so that the capacity

FIGURE 7.

CELL NO. 17 - NINTH CYCLE

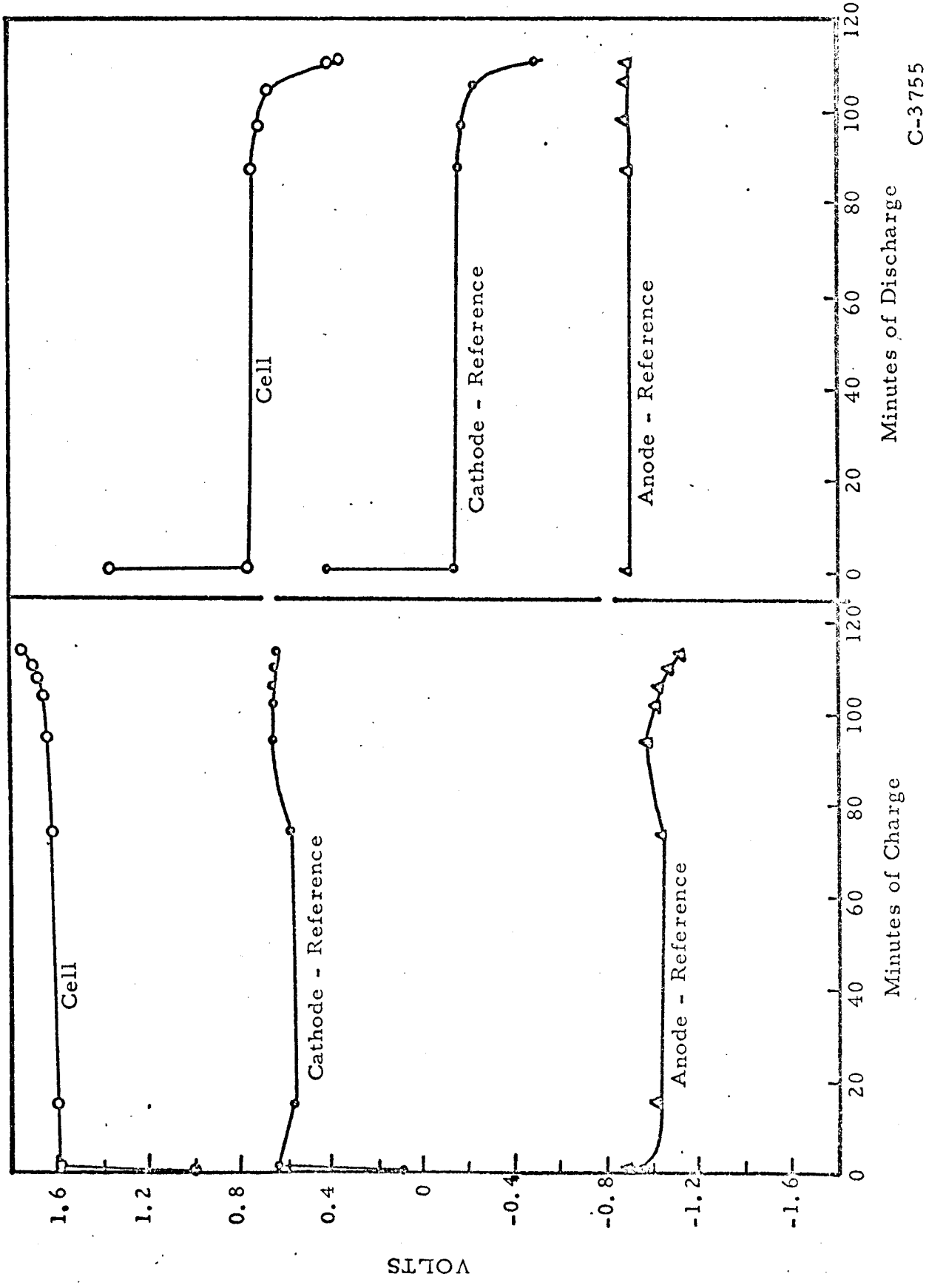
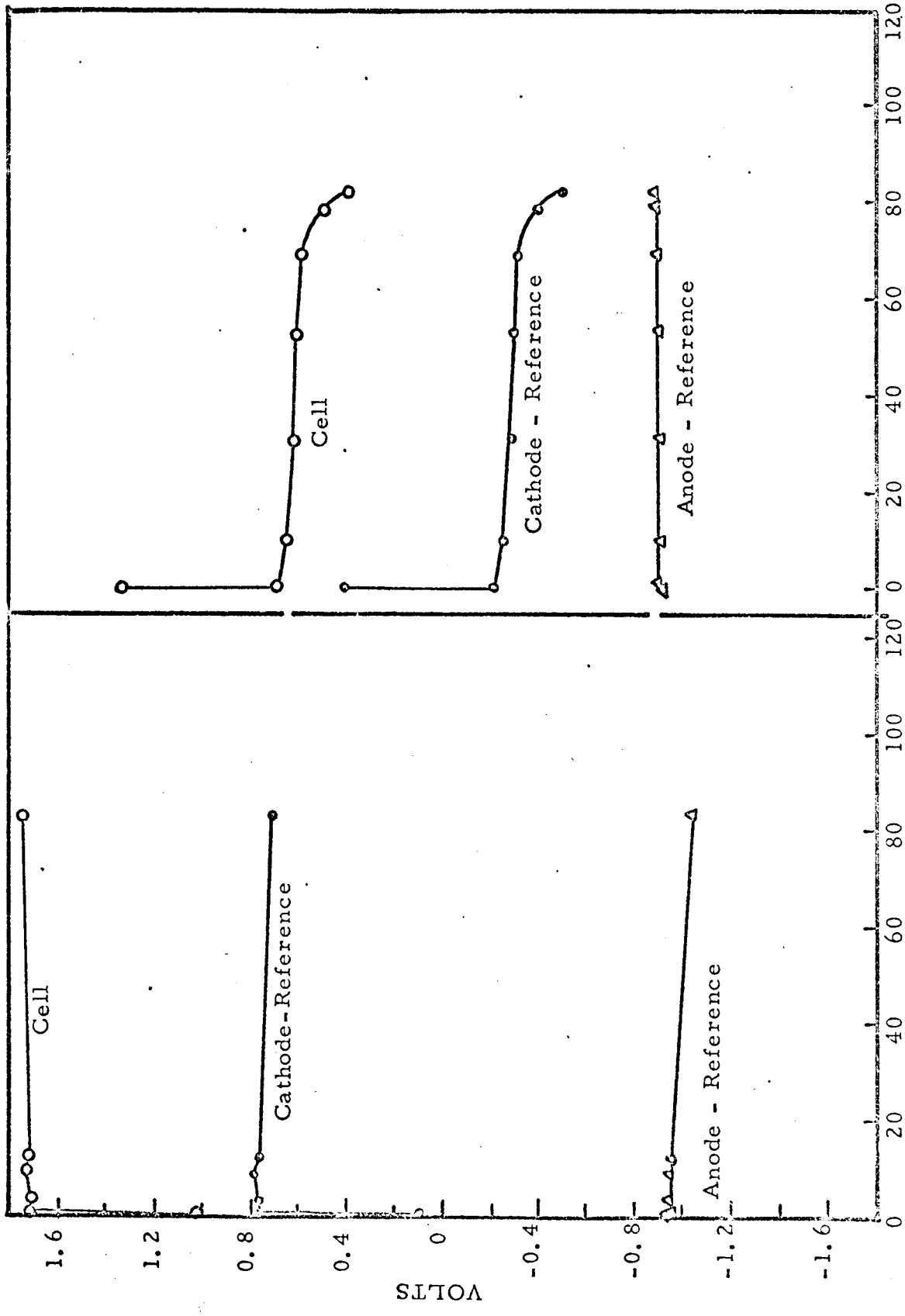


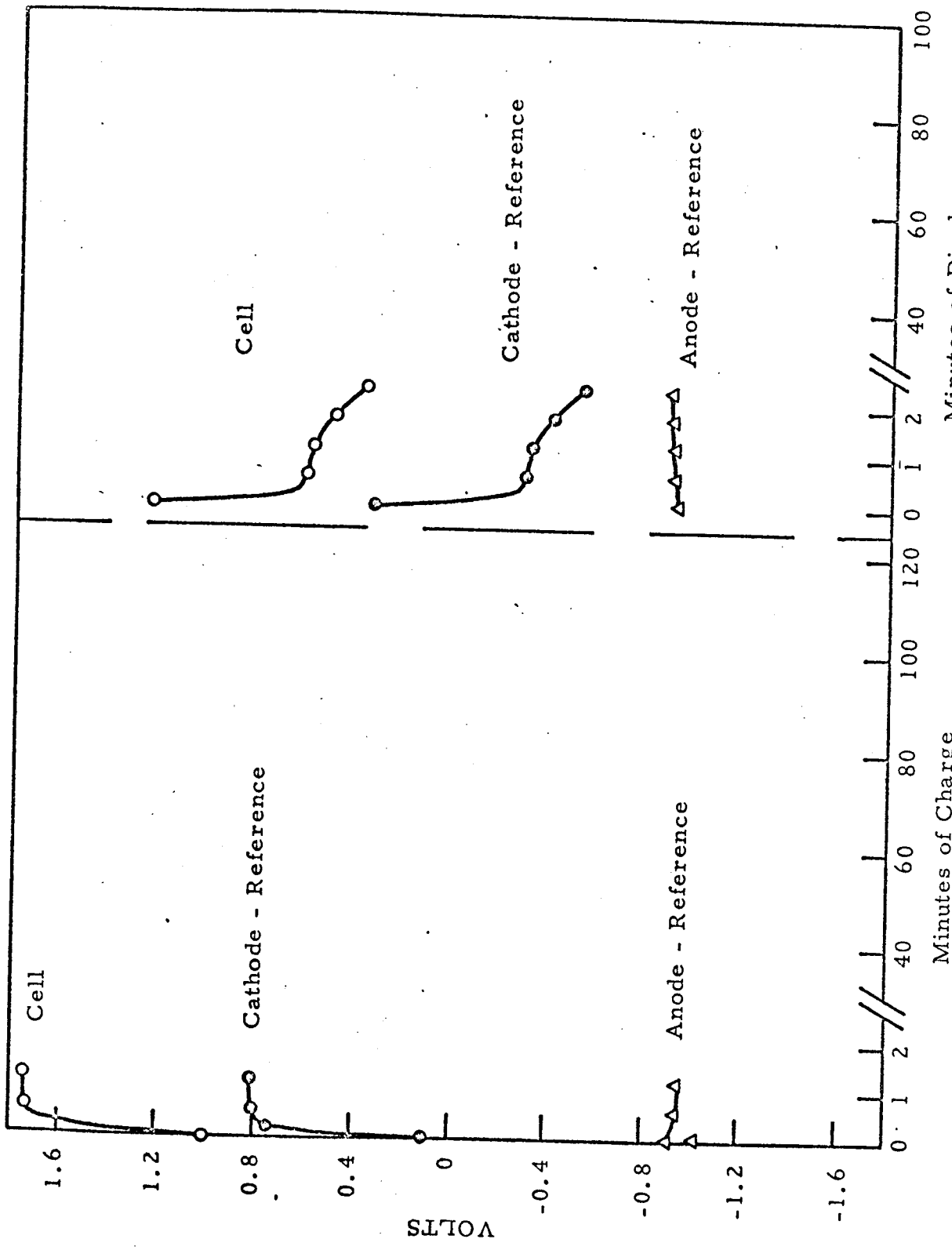
FIGURE 8.

CELL NO. 17 - THIRTEENTH CYCLE



C-3756

FIGURE 9.


CELL NO. 17 - FOURTEENTH CYCLE
Cell
Cathode - Reference
Anode - Reference
VOLTS
1.6
1.2
0.8
0.4
0
-0.4
-0.8
-1.2
-1.6
0 1 2 40 60 80 100 120 0 1 2 40 60 80 100
Minutes of Charge
Minutes of Discharge
C-3941

in terms of watt-hours per pound of active components is greatly increased. Typical charge and discharge curves for cells on the 24-hour regime are shown in Figures 10 and 11. We have had no problems with the oxygen electrodes in either system at this lower current density. The two-electrode cell has completed 15 cycles and the three-electrode cell has completed 39 cycles to date.

TABLE IV.

PERFORMANCE OF SYSTEMS ON TWO-HOUR REGIME PRIOR TO TESTING ON 24-HOUR REGIME

	3-Electrode Cell	2-Electrode Cell
Cd Weight	0.0222 lbs.	0.0206 lbs.
Component Weight[1]	0.127 lbs.	0.174 lbs.
Current Density	11.1 mA/cm^2[2]	11.7 mA/cm^2
Discharge Voltage	0.8 volt	0.82 volt
Input	1.71 amp-hr	1.59 amp-hr
Output	1.68 amp-hr	1.35 amp-hr
Component Output	10.61 W-hr/lb	6.37 W-hr/lb

(1) Components consist of oxygen electrode, electrolyte, cadmium electrode.

(2) All values are average values for total number of cycles completed.

4. Temperature Studies

Unit cells of both the two-electrode and three-electrode systems have been built for testing at 0° and 40°C. The cells will be tested in the environmental facilities of the Union Carbide Computer Test Facility as soon as Testing Stations are available.

TABLE V.

PERFORMANCE OF THE TWO-ELECTRODE SYSTEM ON THE 24-HOUR RATE

Cycle No.	Ampere-Hour Input	Discharge Voltage	Current Density (ma/cm^2)	Ampere-Hour Output	Watt-Hr/lb Component Output (1)
2	1.73	0.895	1.20	1.68	8.65
4	1.92	0.90	1.37	1.88	11.00
8	1.92	0.91	1.37	1.61	8.41
11	1.92	0.91	1.37	1.83	9.59
13	1.87	0.90	1.34	1.79	9.24
15	1.85	0.90	1.32	1.82	9.44

(1) Components consist of oxygen electrode, electrolyte, cadmium electrode.

TABLE VI.

PERFORMANCE OF THE THREE-ELECTRODE SYSTEM ON THE 24-HOUR RATE

Cycle No.	Ampere-Hour Input	Discharge Voltage	Current Density (ma/cm^2)	Ampere-Hour Output	Watt-Hr/lb Component Output (1)
2	2.40	0.90	1.72	2.17	15.40
3	2.40	0.90	1.72	2.12	15.00
7	2.40	0.90	1.56 (2)	2.16	15.30
15	2.40	0.93	1.17	1.64	12.00
33	2.40	0.90	1.39	1.94	13.75
36	2.40	0.89	1.49	2.09	14.65
38	2.23	0.88	1.60	2.19	15.20

(1) Component consists of oxygen electrode, electrolyte and cadmium electrode.

(2) Cell discharged at constant voltage from cycle 7 to 15 inclusive. All others at constant current.

FIGURE 10.

TYPICAL CHARGE AND DISCHARGE CURVES FOR THE TWO-ELECTRODE SYSTEM ON THE 24-HOUR CHARGE/24-HOUR DISCHARGE REGIME

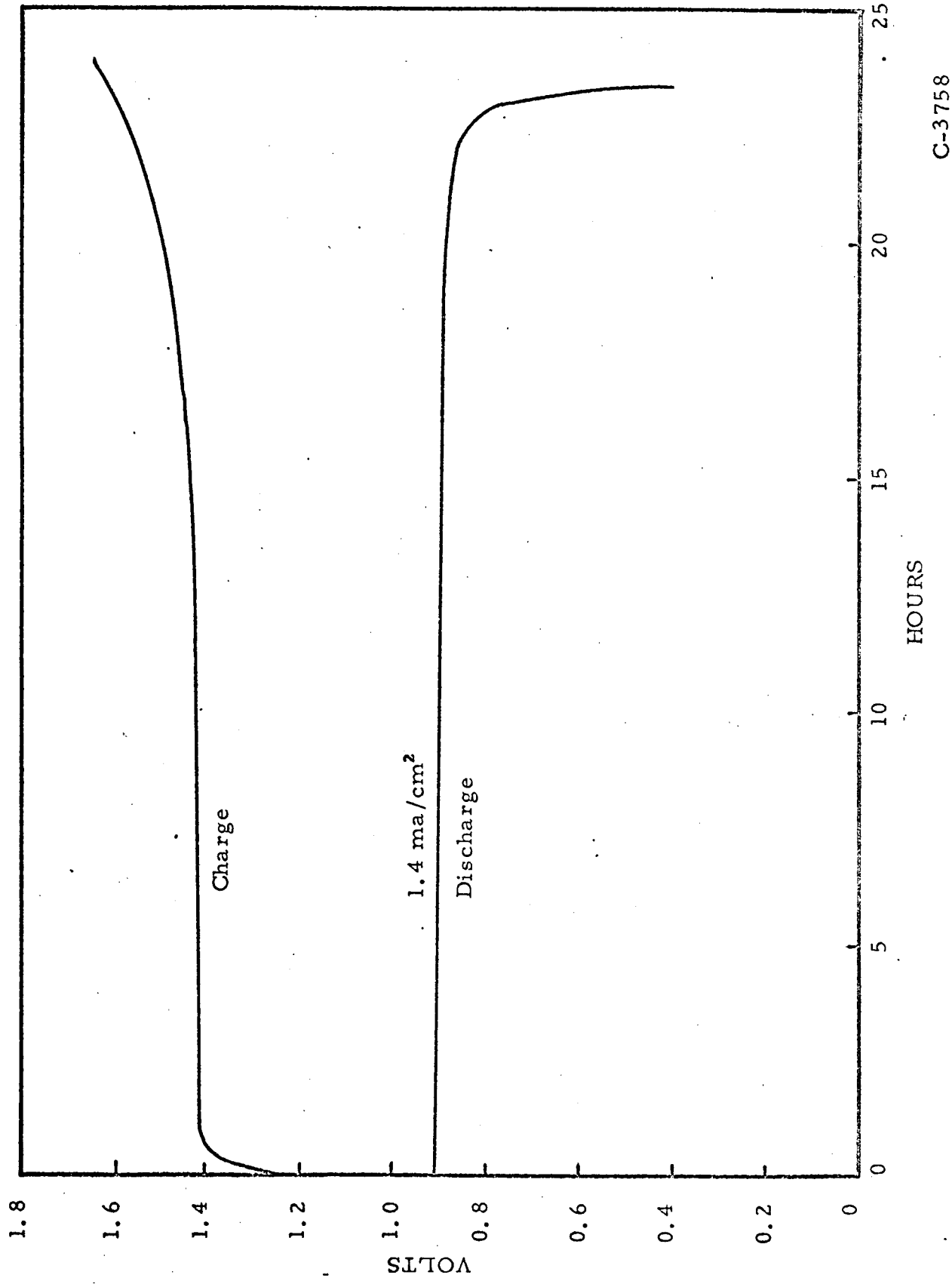
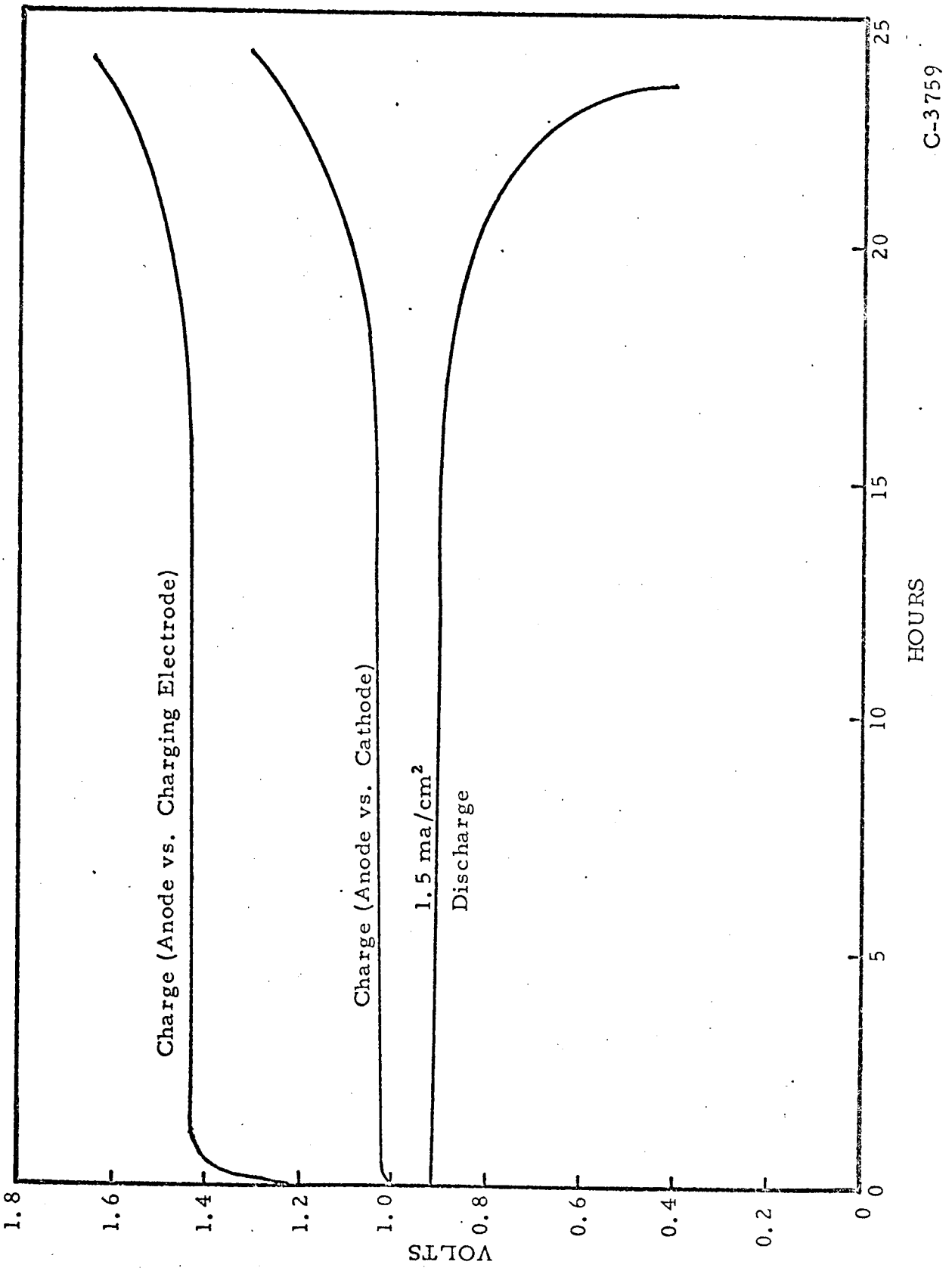


FIGURE 11.

TYPICAL CHARGE AND DISCHARGE CURVES FOR THE THREE-ELECTRODE SYSTEM ON THE 24-HOUR/24-HOUR DISCHARGE REGIME CHARGE



5. High Capacity Anode

Cadmium electrodes containing approximately four times as much cadmium as the presently used electrode have been prepared and are being tested. A three inch square electrode, with cadmium deposited at nine amperes for one hour, has produced an electrode capable of producing one ampere for seven hours or 0.121 amp-hr per square centimeter. Only a few cycles have been completed at this time.

NEW TECHNOLOGY

There are no new technological advances falling within the scope of this contract to be reported at this time.

PROGRAM FOR THE NEXT REPORTING PERIOD

The problems we have had with the American Cyanamid electrode have not been noted in similar work with zinc-oxygen batteries. We plan to make a thorough comparison of the two systems in an attempt to discover the reasons for the oxygen electrode failures. Until we have reason to believe these problems are solved, we will continue our work with the three-electrode system in parallel programs with the American Cyanamid electrode and the Union Carbide electrode.

We plan to freeze on a cell construction and to complete evaluation of the system under the four charge/discharge regimes required. The cell behavior over the specified temperature range of 0° to 40°C will also be explored.

It is believed that an optimum oxygen pressure in the gas space behind the cathode can improve oxygen electrode performance and cycle life. The effect of this factor over a limited range will be evaluated.

CONCLUSIONS AND RECOMMENDATIONS

During the past quarter, work with the two-electrode system has brought to light a problem with the American Cyanamid oxygen electrode. This electrode tends to deteriorate under the stress of the two-hour charge/two-hour discharge regime. The problem is being studied but until causes and solutions for the problem can be found, it is deemed advisable to carry on the work of the program with the three-electrode system.

The polypropylene mat separator previously used as a charging electrode separator does not provide for adequate oxygen evolution during charging. Some form of spacer must be provided which will give a free path for oxygen escape.

In the great majority of cells tested, end of cycle life has been caused by oxygen electrode deterioration. In general, the American Cyanamid electrode has shown better initial performance, but has deteriorated more rapidly, so that in the long run the Union Carbide electrode with the auxiliary electrode has given the longest cycle life. Whether the American Cyanamid electrode will be the better electrode in a three-electrode system remains to be determined. However, we feel it is too early to standardize on one electrode, and we should continue to run parallel programs using both electrodes. A limited study to evaluate the effect of oxygen pressure in the gas space is recommended as a means of extending cycle life of the Union Carbide electrode.

BIBLIOGRAPHY

1. U. S. Patent 3, 320, 139, "A Method for Preparing Negative Electrodes", M. Golben and G. A. Mueller.